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Research paper

Halobismuthates with bis(pyridinium)alkane cations: Correlations in crystal structures and optical properties

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ABSTRACT

A series of four chloro- and bromobismuthates with bis(pyridinium)alkane cations $(Py(CH_2)_nPy)^{2+}(C_n)$ and $(4\text{-}PyH)(CH_2)_n(4\text{-}PyH)^{2+}(H_2C_n)$ were synthesized and characterized. Analysis of their crystal structures, as well as previously reported data, results in establishment of correlations between the type of halobismuthate anion and the nature of cation. Luminescent properties of obtained compounds are reported and discussed.

1. Introduction

Halide complexes of late transition and post-transition metals (in particular, bismuth) evoke a significant interest due to a number of promising physical properties [1,2], including ferroelectricity and ferroelasticity [3–9], thermochromism [10,11], luminescence [12–15], photochromism [16–19] and photocatalytic activity [20–24]. From the point of view of coordination chemistry, an attractive feature of this class of compounds is their remarkable structural diversity [1–2]. Due to the oligomerization via bridging halide ligands, halobismuthates can reach nuclearity of up to 8 Bi (for discrete anions) [24–33], as well as form various, predominantly 1D, polymers [25,34–36] and heterometallic complexes [37–39]. However, synthesis of such complexes cannot be always controlled in a straightforward, i.e. stoichiometric, way: even when well defined amounts of all reagents are used, the final X/metal ratio and the structure of forming halobismuthate will vary and cannot be precisely predicted. It was noted [2,40] that one of the key factors in these processes is the nature (geometry and charge) of cationic part, but the exact correlations are still to be found. The same observations were made also for other metal halide complexes [20–23]. Therefore, information on new halobismuthates, especially within the families of related cations, is needed. The importance of such studies becomes especially evident considering the increasing interest in the iodometalate systems which are widely used in the "perovskite-type" solar cells.

In this work, we present a set of new compounds containing bis(pyridinium)alkane cations with a different number of CH_2 groups between the pyridine rings (C_n) or bis-protonated 1,X-bis(4-pyridinium)alkanes (H_2C_n). These are $(C_3)_3[Bi_2Cl_9]_2$ (**1**), $(H_2C_3)_2[Bi_2Cl_{10}]$ (**2**), $(C_4)_3[BiBr_6]_2$ (**3**) and $(C_5)_3[Bi_2Br_9]_2$ (**4**). All compounds are luminescent (QY up to 5.08%). Tentative correlations between the type of cation and the structure and stoichiometry of the anion, based both on new and previously reported data are discussed, as well as the comparison of optical properties.

2. Experimental section

2.1. General

All chemicals and solvents were of reagent grade. Elemental analysis was performed on a Euro NA 3000 Elemental Analyzer (EuroVector). Bis(pyridinium)propane, butane and pentane dibromide salts (C_3Br_2, C_4Br_2 and C_5Br_2) were obtained by reactions of 2 equivalents of pyridine and 1.15 equivalent of corresponding dibromoalkane in acetonitrile (reflux, 24 h) and identified by ^1H NMR spectra (yield > 90%, see SI for details).

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